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FURTHER INVESTIGATION OF THE DISTRIBUTION OF ATOMIC COBALT IN THE FLAME

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For measuring the exact distribution of metal atoms in the flame, HITACHI 207 atomic absorption spectrophotometer was modified to a single light path with a smaller diameter of the light beam. Using this improved spectrophotometer, the more detailed distribution of cobalt atoms in the air-acetylene flame was measured in terms of some cobalt(III) complexes.

Previously, we studied the interference of various ligands in cobalt(III) complexes to the atomic absorption of cobalt(1). This result suggested that the ligands coordinating to cobalt were essential in determining the atomic absorption of this element. Chakrabarti et al. also pointed out the importance of ligands in atomic absorption spectrometry for the highly oxidizable metals such as Ti, Zr, Hf and Sn(2-4). To elucidate these ligand effects in the flame, it is useful to measure the distribution of atoms in the individual part of the flame, as Rann and Hambly suggested in their earlier work(5). From such a point of view, we measured the distribution of cobalt atoms for cobalt(III) complexes in the flame in our previous paper, where the double light path system with a wide diameter of the light beam from 10 to 15 mm was used(1). It is necessary and interesting, however, to measure the more accurate distribution of atoms in order to discuss precisely the dynamical phenomena in the flame. Hence, we modified the spectrophotometer to make it possible to measure the distribution of atoms in a smaller area of the flame. In the present work, the exact distribution of cobalt atoms for a few complexes is reinvestigated, using the new measuring method.

Since HITACHI 207 atomic absorption spectrophotometer used in this experiment has a double light path through the flame and the apparent diameters of the light beams at the flame are very wide ranging from 10 to 15 mm, the obtained optical data are averaged values at a rather larger part of the flame. Therefore, a spectrophotometer with a single light path system and a smaller diameter of the light beam was required to investigate the accurate distributions of atoms in the flame. For such a purpose, HITACHI 207 atomic absorption spectrophotometer was modified as shown in Figure 1. The burner and the mirror at the front of the entrance slit were removed from the instrument with the double path system, and an optical bench with about 2 m of length was

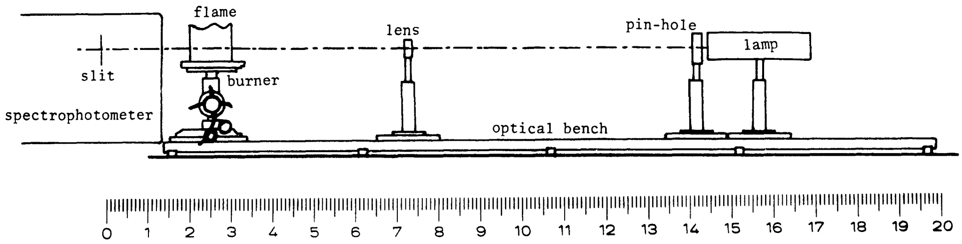

Figure 1
The optical arrangement for the measurement of metal distribution in the flame. The dotted line is the optical axis and the number of the scale is in the unit of decimeter.

attached to the spectrophotometer along the optical axis as shown in Figure 1. The burner was replaced on the bench at the same distance from the entrance slit as the original set-up and a hollow cathode lamp and convex lens were placed at the distance of 130 and 47 cm from the center of the burner, respectively. The light beam of the hollow cathode lamp was made narrower by using a pin-hole of 3 mm diameter placed at the front of the lamp. As the result of this new optical arrangement, the light beam at the flame was sharply reduced to 2 or 3 mm diameter, approximately one fifth of the previous one. The burner used was a 10 cm slot burner, and the flow rate of the air in the analytical flame was maintained at 13 liter/min., and that of the acetylene was varied. The distribution of cobalt atoms was obtained by measuring the absorbances for Co 2432 A line at the thirty different positions of the flame. The selection of each position achieved by moving the burner vertically and horizontally with the screws attached to the burner assembly.

The standard solution of cobalt was prepared by dissolving cobalt metal into dilute hydrochloric acid solution. $K_3[Co(CN)_6]$and $K_3[Co(C_2O_4)_3]$ were prepared according to the ordinary methods(6,7). The purities of these compounds were confirmed by elemental analyses of C, H and N. These compounds were dissolved in water, diluted properly and aspirated into the flame as well as the standard solution.

The distributions of cobalt atoms in the flame for the regular condition, 3 liter acetylene per min., and the acetylene-rich, 4 liter acetylene per min., are shown in Figures 2 and 3, respectively, in terms of the cobalt standard solution, $K_3[Co(CN)_6]$ and $K_3[Co(C_2O_4)_3]$. In the figures, the contour lines show the points in the flame which give the same absorbances, and the areas hatched denote the part of the flame where the absorbances are over O.D. 0.154.

As shown in Figures 2 and 3, each complex has a particular height of maximum absorbance which depends also on the condition of the flame. In the regular condition which is shown in Figure 2 and used in the usual measurement, the point of maximum absorbance for the standard solution is significantly lower than those of $K_3[Co(CN)_6]$ and $K_3[Co(C_2O_4)_3]$. In the acetylene-rich flame, shown in Figure 3, the differences of the points for $K_3[Co(CN)_6]$ and $K_3[Co(C_2O_4)_3]$ are moved far off towards the upper part of the figures. Although maximum height for the standard solution is not so

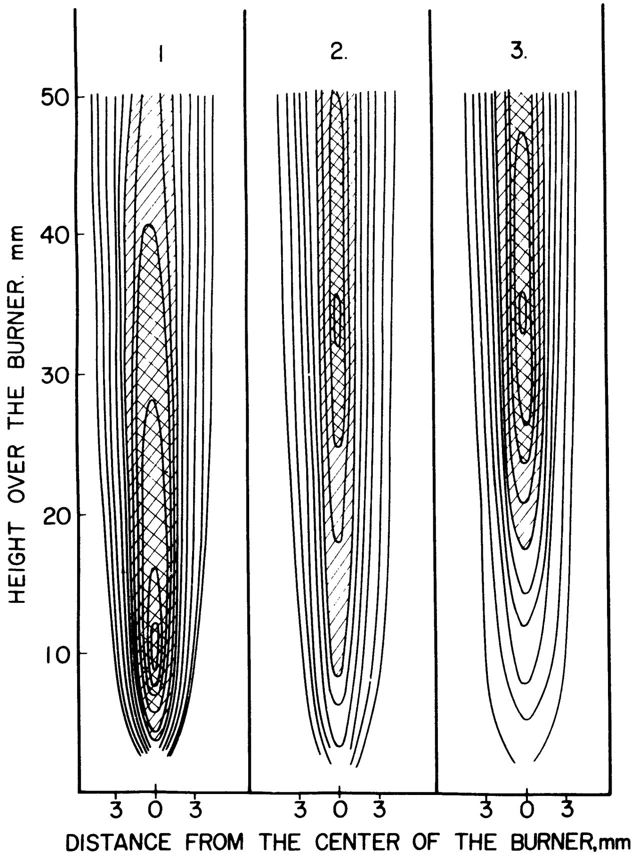

Figure 2
Distributions of atomic cobalts in the regular condition flame.
Acetylene flow rate is 3.0 liter/min.

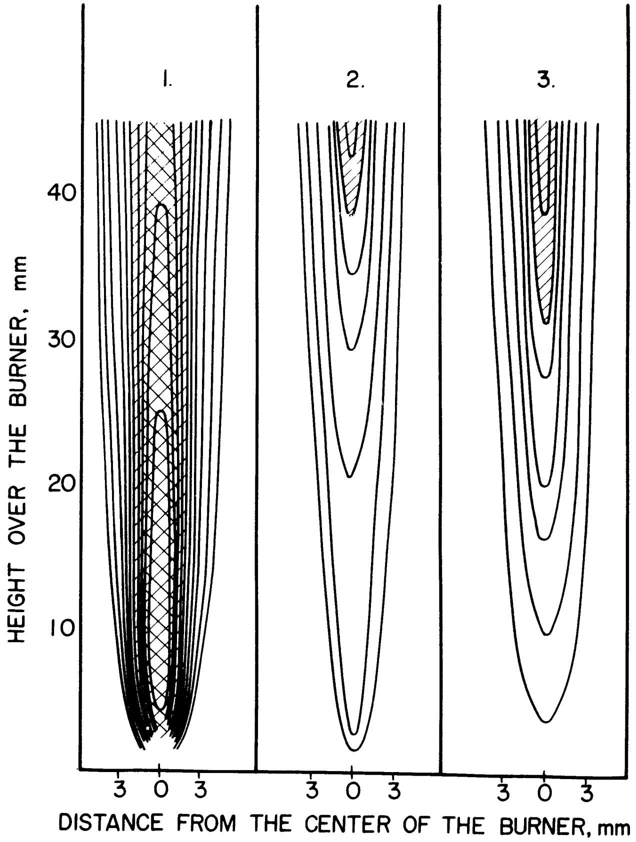

Figure 3
Distributions of atomic cobalts in the acetylene-rich flame.
Acetylene flow rate is 4.0 liter /min.

1. the cobalt standard solution 2. $K_3[Co(CN)_6]$ 3. $K_3[Co(C_2O_4)_3]$
Concentration of cobalt was 30 µg/ml and Co 2432 A line was used. The absorbance increases successively from the outer contour line to the inner, starting with 0 with an interval of O.D. 0.024.

obviously changed with the acetylene-rich flame as $K_3[Co(CN)_6]$ and $K_3[Co(C_2O_4)_3]$ are, it expands upwards somewhat from the point with the normal condition, and stays at the lower middle portion of the flame.

In the previous paper(1), the data were given by the double path method and are the averaged values in the wider part of the flame. Although these data do not exactly reflect the actual aspects of the flame, the difference of the distributions between the standard solution and complexes is observed under the different flame conditions. We also reported that the ligand effect depends on the kind of coordinating atom to the cobalt in its ligand, and that the intensity of this interference decreases in the higher temperature flame and increases in the lower temperature flame such as acetylene-rich. These facts suggest that the pyrolysis of the bond between the central cobalt and coordinating atom is rate determining process of metal atomization in the flame.

These situations are again and more clearly observed in the present experimental figures shown in Figures 2 and 3. The present distributions measured by the single path method reveal the smaller differences between $K_3[Co(CN)_6]$ and $K_3[Co(C_2O_4)_3]$. The atomization processes of them in the flame apparently differ due to the formation of each intermediate compound, carbide for the former and oxide for the latter, which were not evident in the previous observation with the double path system.

On the other hand, the single narrower beam may be inconvenient for the use of routine analysis because the absorbance is changed abruptly against the measuring site in the flame, and the best sensitive area in the flame is very limited comparing to the measurement by the wider beam system of usual commercial apparatus. Furthermore, the signal of the absorbance obtained by the single path system is more susceptible to the ligand comparing to that by the double path system. However, it is obvious that the exact measurement of the metal distribution by the single path system with a narrower beam is indispensable for the quantitative discussion with respect to the reactions which occur in the flame, as was clearly shown by this experiment.

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